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**14. ABSTRACT**

Significant accomplishments were made under the program of dynamical spectroscopy, aimed at elucidating details of chemical dynamics in condensed media. In fact, there now is a well-defined field of multi-dimensional spectroscopy, entirely aimed at the essence of what we had proposed. In the same natural vain of evolution, we developed the rather powerful technique of Time and Frequency Resolved Coherent Anti Stokes Raman Scattering (TFRCARS), as a tool that goes beyond the interrogation of interactions and molecular dynamics in condensed media. This four-wave mixing scheme, with transform limited detection of evolving coherences, can be regarded as a complete experiment in the creation, manipulation, and interrogation of quantum coherences. As such, it foreshadows useful quantum control, be it for chemical or computational purposes. A significant part of our present effort is aimed at devising and implementing control with shaped pulses to demonstrate computational algorithms in the laboratory. The original inspiration for developing TFRCARS was our aim to manipulate molecular wavepackets in regions where direct pumping could not be achieved, due to the inaccessible Franck Condon factors. The target of those studies was the detailed dissection of non-adiabatic dynamics in the condensed phase prototype of solvated molecular iodine. While significant progress has been made toward this end, both direct experimentation and theoretical understanding of this process remain somewhat illusive. Highlights of advances made in theory and experiment are given based on some 20 published works that have appeared during this funding period, as a result of partial or total support by the grant.

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## Final Technical Report, 2001

# Dynamical Spectroscopy of Prototypes in Condensed Phase Chemistry

## AFOSR Grant F49620-98-1-0163

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## ABSTRACT

Significant accomplishments were made under the program of dynamical spectroscopy, aimed at elucidating details of chemical dynamics in condensed media. In fact, there now is a well-defined field of multi-dimensional spectroscopy, entirely aimed at the essence of what we had proposed. In the same natural vain of evolution, we developed the rather powerful technique of Time and Frequency Resolved Coherent Anti Stokes Raman Scattering (TFRCARS), as a tool that goes beyond the interrogation of interactions and molecular dynamics in condensed media. This four-wave mixing scheme, with transform limited detection of evolving coherences, can be regarded as a complete experiment in the creation, manipulation, and interrogation of quantum coherences. As such, it foreshadows useful quantum control, be it for chemical or computational purposes. A significant part of our present effort is aimed at devising and implementing control with shaped pulses to demonstrate computational algorithms in the laboratory. The original inspiration for developing TFRCARS was our aim to manipulate molecular wavepackets in regions where direct pumping could not be achieved, due to the inaccessible Franck-Condon factors. The target of those studies was the detailed dissection of non-adiabatic dynamics in the condensed phase prototype of solvated molecular iodine. While significant progress has been made toward this end, both direct experimentation and theoretical understanding of this process remains somewhat illusive. Highlights of advances made in theory and experiment are given based on some 20 published works that have appeared during this funding period, as a result of partial or total support by the grant.

# I. Accomplishments and New Findings

Many-Body Interactions [1], [4] &[9]: One of the fundamental, outstanding problems in the treatment of chemical dynamics in condensed media is the issue of non-additivity of pair interactions, and corrections therein to construct effective, global, universal, semi-empirical methods that can be economically evaluated. This theme is one that we have developed with some care over the years, under refinements of what is generally referred to as diatomics-in-ionic-systems (DIIS), which is an extension of the diatomics-in-molecules method which explicitly includes couplings to excited ionic states. The most incisive analysis of the method and its generalization is discussed in [9]. There, it is shown that DIIS contains the essence of quantum induction and quantum dispersion, effects that cannot be included in any classical formulation in terms of distributed partial charges and centers of polarization. The most impressive demonstration of the accuracy of the method is in the nontrivial treatments of hydrogen bonded networks: the HF dimer [1], HF clusters [9], and the water molecule [4]. One of the important accomplishments of this approach is the unique interpretation of the stability of atomic oxygen in solid hydrogens [12], an experimental finding of ours which could not be rationalized without the DIIS framework.

Solid hydrogens doped with atomic oxygen [12]: In direct response to the cryogenic HEDM program of the AFOSR, we had carried out studies of O-doped solid $D_2$ and solid $H_2$. While the general results with regard to the ground state $O(^3P)$ atoms were no-controversial, we had also observed that $O(^1D)$ atoms could radiate in the solid without bleaching. This would indicate unusual stability, since the atom-molecule reaction in the gas phase is not activated. As stated above, it was possible through DIIS that a many-body polarization develops in the solid state, one that generates a barrier along the solid state reaction coordinate. More generally, we were able to demonstrate unusual stability of the $O(^3P)$ doped lattice, as evidenced by the fact that the guest diffusion could set until the destruction of the lattice [12]. This stability we had predicted previously, as arising from the increased density of the solid, due to the strong van der Waals forces around the impurity centers. In short, the system fits the requirements of a HEDM, scaling being a nontrivial task that has not yet been dealt with in earnest. We do not pursue these studies at present.

Nonadiabatic Many-Body Dynamics and Quantum Time Correlations in Nonlinear Spectroscopy [2], [6], [10], [14]: Given global descriptions of electronic

manifolds, a second challenge is the treatment of dynamics in multiple electronic surfaces, i.e. chemistry. With the DIIS construct, we have implemented this in the fundamental problem of hole migration, and localization in Helium clusters [6]. This system was chosen for its simplicity, hence the possibility of rigorously testing methods, and the availability of unexplained data on the fragmentation of ionized helium clusters. This nearly exact treatment of coupled electronic nuclear dynamics, has provided deep insights in the general problem of energy relaxation and charge localization in condensed helium, a subject that we have undertaken experimentally. All of the issues involved in non-adiabatic dynamics arise in nonlinear electronic spectroscopies, such as resonant Raman spectroscopy in condensed media [10, 14]. A most elegant theoretical framework for treating this subject in the most explicit time dependent quantum molecular dynamical approach was given in [14]. The method, semi-classical molecular dynamics in coherent state representation we first advanced for linear spectroscopy [2], then adapted for nonlinear spectroscopy along with the diagrammatic tool of time-circuit diagrams [10,14]. The three-time correlation that described the RR process, corresponds to hopping between electronic states in a coherence, propagating forward on bra (ket) states and backward on ket (bra) states, to form closed circuits of multiples of $2\pi$. Here, the radiation field provides the non-adiabatic coupling between electronic states. Using the approach, we have explicitly evaluated the quantum three-time correlation function of a 36 degrees of freedom system, reproducing the experimental RR spectrum of $I_2$ dissolved in liquid Xe. This, I believe is one of the most valuable theoretical developments in spectroscopy, in essence, we know how to evaluate any nonlinear process with interaction potentials as sole input.

Time Frequency Resolved Coherent Anti-Stokes Raman Scattering (TFRCARS) [11], [13], [15], [18], [20]: The four-wave mixing scheme of TFRCARS can be best understood in terms of the time-circuit diagrams mentioned above. The process is a direct three-time time correlation, between coherences and populations that are sequentially prepared by the application of three, non-collinear, fs pulses. In the ost complete implementation, a fourth pulse is used as gate [11], to measure the spectrally-dispersed time-resolved third-order polarization. We have carried out developments of the process in the gas phase, [11, 15], to clearly identify the processes involved, and to map out the optical scattering process in terms of quantum logic gates implemented in the molecular Hilbert space [13]. After showing that the required logic gates for executing arbitrary quantum computing naturally occurs in TFRCARS, we have illustrated how such gates can be put together to carry out an algorithm, and in

particular the Deutsch-Jozsa algorithm which has become a benchmark for such implementations [20]. The method is of course highly useful in interrogations of molecular coherences in condensed media, and we have already implemented this approach in the solid state, to develop a detailed picture of vibrational dephasing in the model system of iodine isolated in rare gas solids [13, 18]. Beside providing a rather complete picture of dephasing through vibration and temperature dependence studies, this 4-wave mixing spectroscopy can be regarded as the first step in carrying out controlled stagings of curve crossings, a target that we intend to pursue along future developments.

Dynamical spectroscopy and prototypes of condensed phase dynamics [3], [5], [8], [17]: A review article on this general subject, with over 400 references was published [5]. The article highlights the general issues, the progress of the field, and charts directions to tackle the fundamental unsolved problems. A significant part of the review outlines the progress achieved in Irvine, and science that has evolved from our lab. The important role of the time resolved approaches is perhaps best illustrated by the example of what can be learned about "Lattice dynamics from the eyes of the chromophore" [3]. There, we illustrate how details of interactions, and nonlinearity of dynamics and dissipation can be discerned directly, and the role of simulations in such developments. A rather incisive tool in the time dependent analysis is laser chirp, which can give vectorial information regarding evolving momenta [8]. More recently, we have also adapted vibrational self-consistent methods for the analysis of lattice dynamics [17], as a most accurate way of describing anharmonicities in the extended systems of interest. This was subsequently used in descriptions of dephasing to be observed through 4-wave mixing schemes [18].

**A quantum bath, superfluid helium [7, 16, 19]:** The most common descriptions of condensed media involve system-bath separations, where the system is developed quantum mechanically while the bath is approximated by various classical, semi-classical, or simply influence functional methods. What happens when the bath is quantum in nature? This begs the unescapable question of describing the many-body quantum mechanics of a quantum bath, and superfluid helium is the naturally occuring Bose condensate that can be experimented with. This we have developed methods for interrogating superfluidity on microscopic scales. In one of the more successful approaches to this problem we developed strong field excitation with fs pulses as the means for ionization, electron-hole recombination, Rydberg state preparation, and the interrogation of these Rydberg excitation centers in optical spectroscopy [7]. We have since developed the theoretical tools for describing interaction potentials of such

excitations with the bath [16], and density functional methods have been adapted for solving the structures and energetics of solvation of such centers in the superfluid [19]. Through time-dependent density functional methods, we have already made significant progress in describing microscopic dynamics in these system, in an effort to be able to simulate the time dependent experiments that have already been carried out. These prototypes of quantum collective dynamics form one of the most exciting areas of current chemical physical research, with far reaching implications.

## II. Publications (1998-2001)

1. Grigorenko, B. L.; Nemukhin, A. V.; and Apkarian, V. A., *J. Chem. Phys.* 108, 4413(1998). "Hydrogen bonding described through diatomics-in-ionic-systems: The HF dimer"

2. Ovchinnikov, M.; and Apkarian, V. A., J. Chem. Phys. 108, 2277 (1998). "Mixed-Order Semiclassical Dynamics in Coherent State Representation: The connection between Phonon Sidebands and Guest - Host Dynamics"

3. Zadoyan, R.; Almy, J.; and Apkarian, V. A.; *J. Chem. Soc. Far. Disc.*, 108, 255 (1997). "Lattice Dynamics from the "Eyes" of the Chromophore: Real-Time Studies of $I_2$ Isolated in Rare Gas Matrices"

4. Grigorenko, B. L.; Nemukhin, A. V.; and Apkarian, V. A., *Chem. Phys.*, 232, 321 (1998). "Towards quantitative diatomics-in-molecules model for the water molecule"

5. Zadoyan, R.; Schwentner, N.; and Apkarian, V. A., *Chem. Phys.* 233, 353 (1998). "Wavepacket diagnosis with chirped probe pulses"

6. Ovchinnikov, M.; Grigorenko, B. L.; Janda, K. C.; and Apkarian, V. A., *J. Chem. Phys.*, 108, 9351 (1998). "Charge localization and fragmentation of ionized helium clusters"

7. Benderskii, A. V.; Zadoyan, R.; Schwentner, N.; and Apkarian, V. A.; J. Chem. Phys. 110, 1542 (1999)."Photodynamics In Superfluid Helium: Femtosecond Laser Induced Ionization, Charge Recombination, And Preparation Of Molecular Rydberg States"

8. Schwentner, N.; Apkarian, V. A.; *Chem. Rev.* 99, 1481-1514 (1999)."Molecular Photodynamics in Rare Gas Solids"

9. Ovchinnikov, M.; Apkarian, V. A.; *J. Chem. Phys. 110*, 9842 (1999)."Practical formulation of accurate many-body potentials through the perturbative extension of diatomics-in-ionic-systems: Applied to HF clusters.

10. Almy, J.; Kizer, K.; Zadoyan, R.; Apkarian, V. A.; *J. Phys. Chem. A 104*, 3508 (2000)."Resonant Raman, Hot and Cold Luminescence of Molecular Iodine in Rare Gas Matrices.

11. Zadoyan, R. and Apkarian, V. A.; *Chem. Phys. Lett 326*, 1(2000)."Imaging the molecular rovibrational coherence through time-gated, frequency-resolved coherent anti-Stokes Raman scattering"

12. Danilychev, A. V., Apkarian, V. A.; Kajihara, H.; Tanaka, S.; Koda, S.; *Low Temp. Phys. 26*, 669 (2000)."Atomic Oxygen in Solid Deuterium."

13. Karavitis, M, Zadoyan, R., Apkarian, V. A., J. Chem. Phys., 114, 4131 (2001). "Time resolved coherent anti-Stokes Raman scattering of $I_2$ in matrix argon: Vibrational dynamics on the ground electronic state"

14. Ovchinnikov, M.; Apkarian, V. A.; Voth, G. A., J. Chem. Phys. 114, 7130-7143, 2001. "Semiclassical molecular dynamics computation of spontaneous light emission in the condensed phase"

15. Zadoyan, R; Kohen, D.; D. Lidar, Apkarian, V. A. Chem. Phys., 266 (2-3), 323-351 (2001). "The Manipulation of massive ro-vibronic superpositions using time-frequency-resolved coherent anti-Stokes Raman scattering (TFRCARS): from quantum control to quantum computing"

16. Eloranta, J. and Apkarian, V. A., J. Chem. Phys. 115, 752 (2001)."The triplet $He_2^*$ Rydberg states and their interaction potentials with ground state He atoms"

17. Bihary, Z.; Gerber, R. B.; Apkarian, V. A., J. Chem. Phys. 115, 2695 (2001)."Vibrational Self-Consistent Field Approach to Anharmonic Spectroscopy of Molecules in Solids: Application to Iodine in Argon Matrix"

18. Bihary,Z.; Karavitis, M.; Gerber, R. B.; and Apkarian, V. A. (in press, 11,2001)."Spectral Inhomogeneity induced by vacancies ad thermal

phonons, and associated observables in time-and frequency-domain nonlinear spectroscopy: $I_2$ isolated in matrix Ar"

19. Eloranta, J., Schwentner, N., Apkarian V. A.; J. Chem. Phys. (submitted, 2001). "Structure ad Dynamics of $He_2$* Bubble-States in Superfluid $^4He$"

20. Bihary, Z. Glenn, D. R., Lidar, D. A., and Apkarian, V. A. (PRL, submitted, 2001)."An implementation of the Deutsch-Jozsa Algorithm on Molecular Vibronic Coherences Through Four-Wave Mixing: A Theoretical Study"

## III. Personnel Supported (9/97 - 3/2001)

Dr. V. A. Apkarian, PI
Dr. D. Tannor, Visiting Professor (one month)
Dr. R. Zadoyan, Postdoctoral Associate
Dr. A. V. Benderskii, Postdoctoral Fellow
Dr. Mika Pettersson, Visiting Postdoc
Michael Karavitis, Graduate Student
Robert Borwick, Undergraduate Student
Areg Boyamyan, Lab Assistant

## IV. Invited Presentations

9/97 Am. Chem. Soc. National Meeting (Las Vegas, Nevada)"Dynamical Spectroscopy of Many-Body Interactions"

9/97 Chem. Phys. Institute, Univ. of Oregon, Annual Retreat (Charleston, Oregon)"Dynamical Spectroscopy of Many-Body Interactions"

10/97 Am. Chem. Soc. Western Regional Meeting (Irvine, CA) "Coherent Nonadiabatic Dynamics in Condensed Phase"

11/97 University of Illinois, Champaign-Urbana (Urbana, IL)"Connecting Spectral Observables to Molecular Motions in Condensed Media"

12/97 Faraday Discussion (University of Sussex, UK) "Non-additivity Interactions and Dynamics in Condensed Media"

1/98 SPIE: Photonics West (San Jose, CA) "Femtosecond Laser Excitation and Spectroscopy of Liquid Helium"

2/98 Bat-Sheva Seminar on Light Induced Reactions in Condensed Phase (Dead Sea, Israel) "Dynamical Spectroscopy of Many-Body Interactions"

3/98 Texas Tech University (Lubbock, TX) "Dynamical Spectroscopy of Many-Body Interactions"

5/98 Molecular Dynamics Contractors Meeting (Monterey, CA)"Towards a Microscopic Understanding of Superfluidity"

5/98 Molecular Dynamics Contractors Meeting (Monterey, CA) "Towards a Microscopic Understanding of Superfluidity"

5/98 Informal Photochemistry Conference (Pasadena, CA) "Matrix Isolated Dynamics"

11/98 University of California, Los Angeles (Los Angeles, CA) "Coherences in the Bath, from Classical to Quantum"

11/98 Free University of Berlin (Berlin, Germany) "Coherences in the Bath, from Classical to Quantum"

12/98 Yale University (New Haven, CT) "Coherences in the Bath, from Classical to Quantum"

2/99 Argonne National Laboratory (Argonne, IL) Many-body interactions and dynamics

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| 3/99 | American Physical Society (Atlanta, GA)<br>"Coherences in the Bath, from Classical to Quantum" |
| 5/99 | ISIS Seminar (UCI, CA)<br>Superfluidity on Molecular Scales, in Real Time |
| 7/99 | Gordon Conf. on Liquids (New Hampshire)<br>Solvation and Dissipation Dynamics in a Quantum Solvent |
| 8/99 | ACS National Meeting (New Orleans)<br>Non-adiabatic dynamics in many-body systems |
| 10/99 | Stanford University (Palo Alto, CA)<br>Superfluidity on Molecular Scales, in real time |
| 2/00 | Cal State Northridge (Northridge CA)<br>Implications of superfluidity on Molecular Scales |
| 5/00 | Boston University (Boston, Mass)<br>From Time & Frequency Domain Spectra to Atomistic Dynamics |
| 6/00 | IV workshop on Quantum Fluid Clusters (Schloss Ringberg, Germany)<br>"Superfluidity on molecular scales, in real time" |
| 7/00 | Free University of Berlin (Berlin, Germany)<br>Time- Frequency-resolved Coherent Anti-Stokes Raman Scattering (TFRCARS): Preparation, Manipulation and Interrogation of molecular coherences |
| 8/00 | Int. Conf. on Cryocrystals and Quantum Crystals (Szklarska Poreba, Poland)<br>Interrogation of Superfluidity on Molecular Scales, in Real-Time |
| 8/00 | ACS National Meeting (Washigton DC)<br>Interrogation of Superfluidity on Molecular Scales, in Real-Time<br>V.A.A., A. Benderskii, J. Eloranta |
| 8/00 | ACS National Meeting (Washigton DC)<br>Applications of Strong Fields in Condensed Matter<br>V.A.A., A. Benderskii, et al. |
| 9/00 | USC (Los Angeles CA)<br>Superfluidity on molecular scales, in real-time |
| 10/00 | U. of Chicago (Chicago, IL)<br>Superfluidity on molecular scales, in real-time |
| 2/01 | Cal State Long Beach (Long Beach CA)<br>Implications of superfluidity on Molecular Scales |

2/01 Sixth Symposium on Molecular Reaction Dynamics in Condensed Matter (Newport Beach, CA)
The manipulation of massive molecular coherences, from quantum control to quantum computing